

## Shipboard System for Transportation of Natural Gas in Zeolites

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TITLE OF THE INVENTION

Shipboard System For Transportation Of Natural Gas In Zeolites

CROSS-REFERENCE TO RELATED APPLICATIONS

Not Applicable.

5 STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR  
DEVELOPMENT

Not Applicable.

REFERENCE TO A "SEQUENTIAL LISTING," A TABLE, OR A COMPUTER  
PROGRAM LISTING APPENDIX SUBMITTED ON A COMPACT DISC

10 Not Applicable.

BACKGROUND OF THE INVENTION

There is no need to emphasize the importance of natural gas as an energy resource. Its steady and growing consumption secures short and long term demand worldwide. It must be realized, however, that due to overall concerns for favorable economics, the presently available transportation technologies for natural gas have to  
15 be considered worthless for many relatively small, and often large but remotely located, gas fields (known also as "stranded gas"). A large worldwide resource of "stranded" natural gas is presently uneconomic due to the prohibitive costs of available methods to bring that gas to market. Pipelines are required for the transportation of natural gas  
20 from the wellhead to onshore markets. The predominant sea-borne transportation

system for natural gas is via liquefied natural gas (LNG) systems. These systems are burdened by high capital cost due to their requirement for a cryogenic liquefaction plant, expensive and require specialized transport vessels, and a regasification terminal at the destination. Although plans exist for floating liquefaction facilities, all present-day  
5 liquefaction facilities are land-based, rendering the transportation costs for gas produced from remote offshore gas fields prohibitive.

Because of their great capital cost, onshore or floating LNG facilities generally require the dedication of very large reserves on the order several trillion cubic feet before transportation becomes economical. Smaller gas reserves are therefore  
10 "stranded" for lack of a less expensive means of transportation.

Recent alternatives to LNG for sea-borne transportation of smaller quantities of natural gas have been proposed. One such method, described in US Patent 6,339,996, incorporated by reference herein, uses a number of composite pressure vessels to store highly compressed natural gas. A second technique, described in US Patent 5,839,383,  
15 also incorporated by reference herein, provides for transportation of highly compressed natural gas (CNG) in coils of continuous high-strength pipe.

By eliminating the need for expensive liquefaction facilities, both methods significantly reduce the capital expenditure required for the sea-borne transportation of natural gas, allowing smaller accumulations to be developed than would otherwise be  
20 economic. Unfortunately, both techniques require the compression of natural gas to very high pressures, typically about 3,000 psi. These high pressures entail

considerable expense and hazard, since rupture of the storage vessels results in the explosive release of the potential energy of compression.

#### FIELD OF THE INVENTION

The present invention relates to an apparatus and methods for the sea-borne transportation and storage of compressed gasses that may include natural gas, carbon dioxide, or hydrogen.

#### DESCRIPTION OF RELATED ART

The related art is summarized in the following patents. The full disclosures of the following patents are incorporated into this patent by this reference:

- 6,339,996 Natural gas composition transport system and method
- 5,839,383 Ship based gas transport system
- 4,619,225 Apparatus for storage of compressed gas at ambient temperature

#### BRIEF SUMMARY OF THE INVENTION

The present invention comprises a system for transporting compressed gas aboard a ship, the system comprising: a) tanks aboard the ship adapted for carrying the compressed gas; b) a zeolite material in each of the tanks, the zeolite material adapted for adsorption of the gas into pore spaces of the zeolite material; and c) connection means for connecting the tanks to sources for receiving and dispensing the gas.

The present invention also comprises a method for transportation of natural gas aboard a ship, the method comprising the steps of:

- a. providing a plurality of tanks on board the ship;
- b. putting a zeolite material in the tanks;

- c. connecting gas delivery tubes to the tanks;
- d. introducing the gas into the tanks under pressure until a desired pressure is reached;
- e. disconnecting the gas delivery tubes to the tanks, and allowing the ship to  
5 embark to its desired destination; and
- f. after the ship reaches its desired destination, connecting gas delivery tubes to the tanks, and discharging the gas from the tanks.

An advantage of the present invention is that it utilizes the adsorption properties of zeolite material to increase the capacity for storing gas on board a ship, and  
10 decrease the pressure required to store the gas. Clathrates, also known as gas or methane hydrates, may also be used for this purpose.

Other advantageous features of the present invention are that the zeolite material is benign, non-toxic, abundant, inexpensive, easily adsorbing under pressure and, when depressurized, easily release methane and other hydrocarbon gases at controllable flow  
15 rates. Important safety advantages of transporting compressed gases adsorbed into zeolite material include lower storage pressures and much slower release of gas if the storage vessel is accidentally ruptured, as more fully described in US Patent 4,619,225, incorporated into this patent by this reference. The lower pressure required for adsorptive storage of natural gas in zeolite material allows lighter, less expensive gas  
20 cargo tanks to be employed than those required for highly compressed natural gas. Because zeolites are highly porous, after initial high pressure required for complete

saturation with natural gas, subsequent maintenance is at a relatively low pressure and high-volume capacity. This feature considerably reduces the costs of ship design, construction, and operation.

Although the volumetric ratio of gas, particularly as liquefied natural gas (LNG), gas-to-liquid (GTL), and compressed natural gas (CNG) technologies, is higher than in the present invention, the present invention has the advantages of loading and unloading simplicity, and almost hazardless storage and shipment of gas in containers filled with inexpensive zeolite material.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a plan view of a ship having gas cargo tanks filled with zeolite material containing natural gas,

FIG. 2 is a profile of the ship depicted in FIG 1, partly cut away to show the gas cargo  
5 tanks filled with the zeolite material, and

FIG. 3 is schematic view of one of the gas cargo tanks depicted in FIG. 1, partly showing external and internal (perforated) pipelines for gas delivery and discharge, and separate cooling and heating systems.

## DETAILED DESCRIPTION OF THE INVENTION

The ship of the present system may be either a shuttle cargo carrier or any other ship suitable for the transportation of bulk cargo. Referring to FIGS. 1 and 2, a cargo ship 1 includes a plurality of compartments or cargo holding areas 2 in which are gas cargo tanks 3 filled with zeolite material 4. For specific compositions of natural gas, the zeolite material 4, prior to its loading into the gas cargo tanks 3, is accordingly grained, modified with an appropriate mole-ratio of hydrochloric acid, dehumidified, and sieved, as is well understood by those skilled in the art, and as disclosed in the following U.S. Patents, which are incorporated into this patent by this reference: No. 4,619,225; No. 6,339,996 B1; and No. 5,247,971.

After loading of the natural gas into the tanks 3 most of the natural gas is adsorbed into the pore space of the zeolite material 4. Adsorption into the inter-crystalline porosity of the zeolites lattice and cavity systems occurs during loading of the gas. Each holding area 2 contains a plurality of gas cargo tanks 3. Thick, strong separation walls 5 separate the holding areas 2 from each other. Division walls 6 separate the gas cargo tanks 3 from each other. Each gas cargo tank 3 is equipped with appropriately strong external walls 7 and tops 8. The tops 8 are pyramidal shapes, with 10 – 15° slopes, and are equipped with suitable hatches 9 for easy filling and vacuuming out of the zeolite material 4.

Referring now to FIG. 3, a gas source terminal 14, through manifolds 12, high-pressure gas pump 11, and piping 10, connects to the gas cargo tanks 3. The same



5        piping 10, in combination with a vacuum pump 13 and manifolds 12, is used for discharge of the natural gas, to storage containers 15, which collectively are also known as a discharge terminal. In an alternate embodiment, a gas pipeline distribution system replaces the storage containers 15.

10        The piping 10 and manifolds 12 are designed to permit easy loading of the natural gas at the gas source terminal 14, and unloading at the storage containers 15, and may be constructed as described in U.S. Patent No. 6,339,996, which is incorporated by reference. An advantage of the present invention is that valves 16 for regulation of cooling and heating-related pressure, piping 10, and manifolds 12 can be designed for much lower duty pressures than the 2,000 to 3,000 psi required in the device described in U.S. Patent No. 6,339,996, because the adsorptive properties of the zeolites allow storage of large volumes of gas at lower storage pressures than achievable through gas compression alone.

15        For sea-borne transportation of natural gas, the ship 1 docks at a production facility or other gas source terminal 14, where compressed natural gas is delivered to the ship 1 at the required rate and pressure. Natural gas is loaded into the cargo tanks 3 through the piping 10 and the manifolds 12.

20        Because charge (loading) of natural gas into the zeolite material is an exothermic process and its discharge (unloading) is therefore endothermic, a heating and cooling system 18 and manifolds appropriately offset and regulate both operations. As is well understood by those skilled in the art, several design choices for cooling and heating,

including either electric cooler/heater installations, cold water, or steam circulation pipeline systems are possible.

As illustrated in FIG. 3, a perforated pipeline system 19 distributes gas, injected by the pump 11, at pressures up to 3,000 psi within a gas cargo tank 3, which is FIG. 3. Gas is discharged from the cargo tank 3 by releasing the pressure and vacuuming it out with the vacuum pump 13 to the maximum economically feasible extent.

Adequately sensitive manometers 20 measure and record the amount of gas delivered into and discharged from the gas cargo tanks. Pressure gages 21 measure and continuously record pressure inside the gas cargo tanks 3. Thermometers 22 with extended temperature sensors are installed for measurement and recording of the temperatures inside the gas cargo tanks 3. The pressure and temperature that need to be applied for loading of natural gas into the zeolite material 4 are generally similar to that which is required for formation and stabilization of gas hydrates.

Because the gas cargo tanks 3 should be completely filled with the adequately grained zeolite material 4, which can compact over time, a level indicator 23 is used to monitor the level of the zeolite material 4.

After high-pressure gas loading, adsorption of the gas into the zeolite material 4 equalizes the pressure in a gas cargo tank 3 to a value near 500 psi. Pressure relief valves are installed for improved safety. Separate sets of pressure supply and discharge valves 24 and 25 respectively are installed for loading from gas delivery

source and for its discharge from gas cargo tanks into off-take pipelines and distribution systems at the storage containers 15.

Because release of pressure is an endothermic reaction, a controlled discharge must be employed to prevent liquefaction or freezing of the discharged gas. After reaching ambient temperature and pressure, the remaining amount of gas, still trapped in the nanoporous zeolite material 4, is vacuumed out. After discharge of at least 90% of gas, the loading and discharging gas valves 24 and 25 are closed, and the ship will return for another load of gas.

Natural zeolite material, the preferred adsorptive storage medium of this invention, are hydrated alumino-silicates of alkaline earth metals. Zeolite structures are characterized by the presence of systems of interconnected cavities. Zeolite material allow the adsorption of large quantities of natural gas onto their internal crystallographic framework structure.

Although zeolites and clathrates are of totally different chemical composition, natural gas can be trapped and compressed in either of their voids at a volumetric ratio of gas as high as 200:1, relative to normal ambient conditions. The present invention provides a ship containing totally sealed gas cargo tanks 3, filled with highly porous, therefore very low specific gravity zeolite material, which can be saturated under moderate pressure with dehydrated natural gas.

An advantageous feature of the present invention is that the same zeolite material will be used for storage and transportation of natural gas many times.

Nevertheless, if necessary, they can be replaced by another load of an appropriate zeolite material.

The amount of natural gas that can be stored and transported is a function of both the composition of the zeolite material employed in the tank and the pressure and temperature used to store the natural gas. In the preferred embodiment, the ship 1 has five main compartments or holding areas<sup>2</sup>, each approximately 45 meters in length and 40 meters wide. The center three compartments are rectangular and are 45 x 40 meters. The bow and stern holds are 45 meters in length, with a slightly tapered width of 30 meters at the forward and aft perpendiculars. This provides approximately 225 meters of longitudinal cargo space. The remaining approximately 59 meters are comprised of the forecastle and the engine/mechanical facilities.

This configuration of the ship 1 results in a total of 80 gas cargo tanks<sup>3</sup> in five compartments. The number of the tanks and their dimensions will be subject of engineering design well known to those skilled in the art, and are functions of the desired shipboard cargo volume capacity and deadweight tonnage ("dwt") of the cargo ship. An exemplary configuration employs a shipboard cargo capacity of 138,000 dwt, and a gross cargo volume capacity of 138,000 cubic meters. However, net cargo capacity will be smaller because of dead space between cargo compartments and machinery necessary for the propulsion of the ship, and the loading and unloading of its cargo. The aforementioned 138,000 dwt carrier, with appropriately-chosen zeolite

material, will have a total gas cargo capacity of approximately 400 million cubic feet, or about 11 million cubic meters of natural gas.

Although the preferred embodiment of the present invention has been described above, it will be understood by those skilled in the art that numerous modifications from the present invention may be made without departing from the scope and meaning of the claims that follow.